Skutterudites: a New Class of Prom sing Thermoelectric Materials

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ABSTRACT

Based on literature data and experimental findings at (IIC Jet Propulsion Laboratory (JPL), semiconductors with the skutterudite structure TPn_3 (where T is a transition metal element such as Co, Rh, Ir, Ni and Pd, and Pn is a pnicogen clement such as P, As and Sb) possess attractive characteristics and show a good potential for high ZT values. The high degree of covalency results in high mobility and low electrical resistivity values while a relatively complex 32 atom unit cell results in a reasonably low thermal conductivity. Both n-type and p-type electrical conductivity samples have been obtained. Room temperature Seebeck coefficient values up to 200 μVK^{-1} for p-type and up to -600 μVK^{-1} for n-type have also been measured on several of these materials. In addition, the large number of isostructural compounds, solid solutions and related phases offer many possibilities for optimization of the transport properties to a specific temperat ure range of thermoelectric applications. By replacing the transition metal or the pnicogen atom by two of its neighboring elements and ensuring that the number of valence electrons is retained, many ternary phases can be successfully derived from the original $CoAs_3$ skutterudite structure. Some of these materials were found to have substantially lower thermal conductivities compared to those of the binary compounds. The composition, band gap and doping level can bc tailored to achieve maximum performance. An overview of the results obtained to date is provided and our approache to achieving high ZT materials arc discussed in this paper.

1NTRODUCTION

Most of the thermoelectric effort of the last 35 years has been devoted to established state-of-the-ad materials: Bi_2Te_3-based alloys, PbTe-based alloys and $Si_{1-x}Ge_x$ alloys. Other well known materials such as n-type Bi-Sb alloys, p-type TAGS and $FeSi_2$ have interesting thermoelectric properties but are used less because of various practical difficulties (high sublimation rates, poor mechanical strength, absence of homologous n-type or p-type

material, low ZT...). Although significant improvements of the thermoelectric properties of these materials have been achieved, a value of one is the current approximate limit for ZT over the whole 100-1 S00 K temperature range. Despite all of the advantages of thermoelectrics as solid state devices, their low energy conversion efficiency greatly limits their performance and thus their range of applications.

Much larger values of ZT are theoretically possible and the investigation of new classes of materials is one of the promising approaches for future research and development of the field of thermoelectric. Indeed, recent progress in solid state physics and materials science could make good use of the various selection criteria (such as a complex crystal structure, heavy atomic components, highl y covalent atomic bonds...) in order to identify new potential candidates,

A systematic search for new thermoelectric materials was started at JPL several years ago and resulted in the identification of a family of compounds with the skutterudite crystal structure as good candidates for high performance conversion efficiency [1]. The skutterudite structure was originally attributed to a mineral from Skutterud (Norway) with a general formula $(Fe,Co,Ni)As_3$ [2]. The skutterudite structure (cubic space group $Im3$, prototype $CoAs_3$) is illustrated in Figure 1. The unit cell contains 8 AB_3 groups.

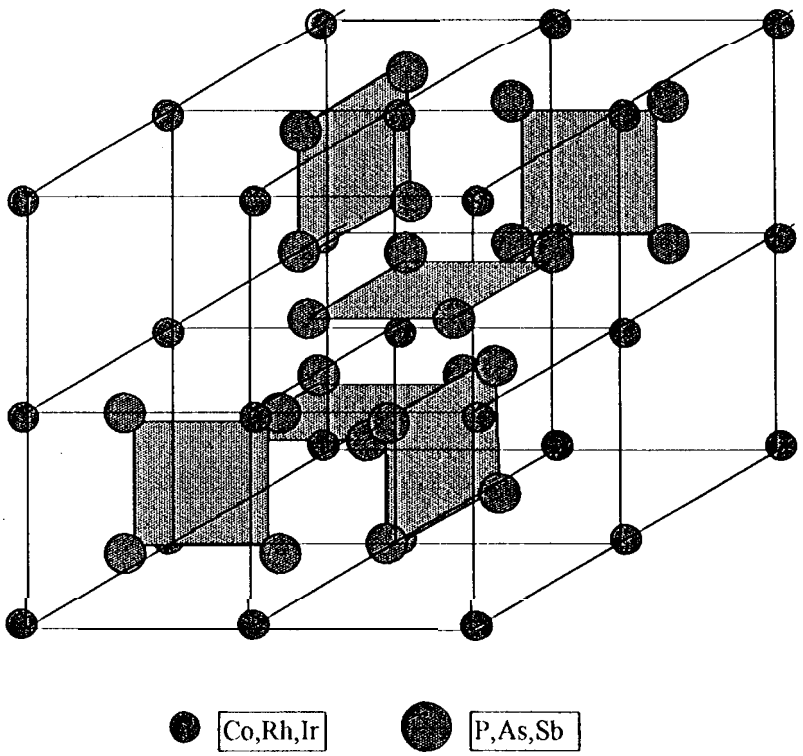


Figure 1: The skutterudite unit cell of formula TPn_3 (T = transition metal, Pn = pnicogen).

It has been shown that the bonding is predominantly covalent in the skutterudite structure [3] and high carrier nobilities have been measured on several skutterudite compounds: $IrSb_3$ [4], $RhSb_3$ [5] and RhP_3 [6]. The unit cell is relatively large and contains 32 atoms which indicates that a low lattice" thermal conductivity might be possible. For the state of the art thermoelectric materials such as PbTe and Bi_2Te_3 alloys, the number of isostructural compounds is limited and the possibilities to optimize their properties for maximum performance in different temperature ranges of operation are also very limited. This is not the case for skutterudites which show a variety of melting points, band gaps and compositions which offers the possibility to optimize composition and doping level for a specific temperature range. Some skutterudite compounds, solid solutions and related phases are reviewed in the following sections.

BINARY SKUTTERUDITE COMPOUNDS

Binary skutterudite compounds are formed with all nine possible combinations of the elements Co, Rh, Ir with P, As, Sb. In this structure each metal atom has six bonds to a pnicogen and each of three pnicogens has two bonds to another pnicogen. Thus, each bond has two electrons which is consistent with the fact that they are diamagnetic semiconductors [7]. Known values for the peritectic decomposition temperature and band gap of these nine binary compounds are reported in Figure 2. Decomposition temperatures for CoP_3, RhP_3, $RhAs_3$, IrP_3 and $IrAs_3$ are only lower limit estimates. We have calculated the band gap values of $IrSb_3$, $CoSb_3$, $RhSb_3$, $RhAs_3$ and CoP_3 from high temperature Hall effect measurements. The only other binary skutterudites known are NiP_3 and PdP_3 which have one more electron valence per formula unit and consequently show metallic conduction [8].

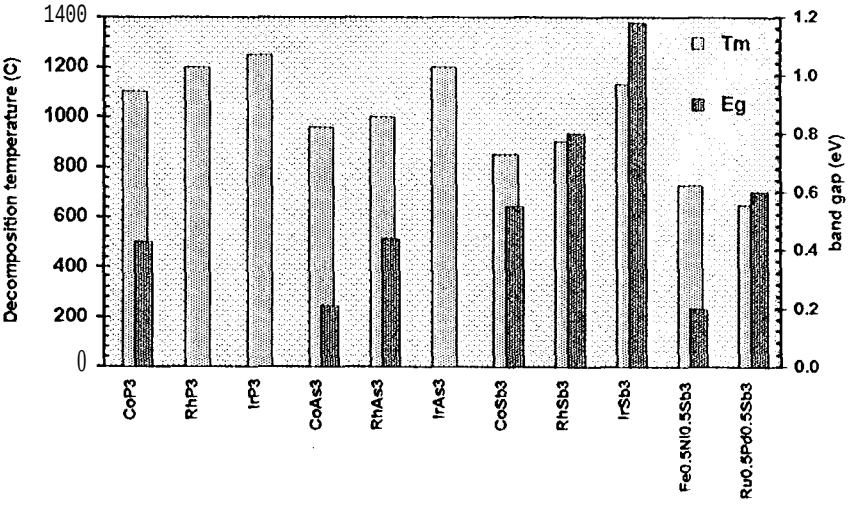


Figure 2: Known values for the decomposition temperature and band gap of the nine binary skutterudites.

The room temperature Hall mobility for several p-type binary skutterudite compounds as a function of the Hall carrier concentration is displayed on Figure 3. The results obtained for $CoAs_3$ and RhP_3 were found in references [9] and [6], respectively. Values for state-of-the-art semiconductors were also included for comparison. It is clear that the skutterudite compounds have exceptionally high hole nobilities, substantially higher than state-of-the-art semiconductors for a given carrier concentration, We have measured a Hall mobility value close to 8000 $cm^2.V^{-1}s^{-1}$ on a p-type $RhSb_3$ single crystal with a Hall carrier concentration of about $3.5x10^{18}$ cm^{-3}. This is the highest p-type mobility ever measured at this doping level. All skutterudites seem to have these high hole nobilities which make them very interesting materials

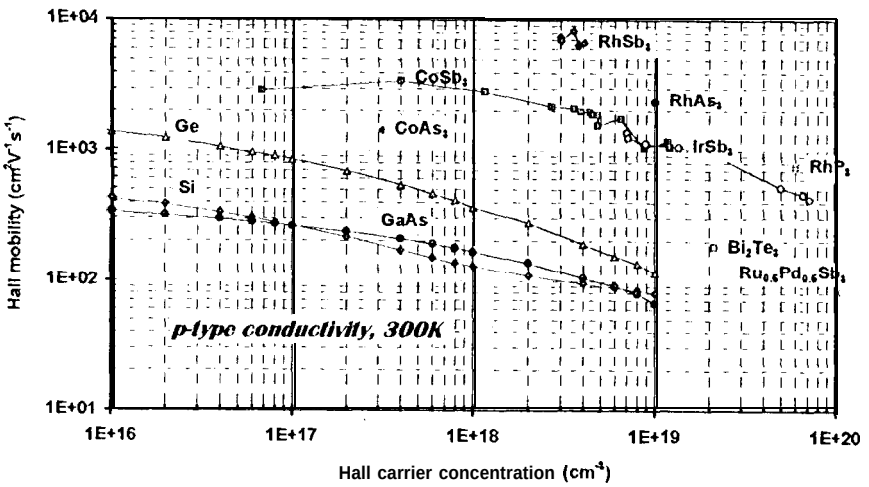


Figure 3: Room temperature p-type Hall mobility as a function of the carrier concentration for several skutterudite compounds. Values for state-of-the-art semiconductors have been included for comparison.

N-type samples have been obtained for $CoSb_3$ and $1rSb_3$ by doping with elements such as Ni, Pd, Pt and Te [10, 11]. The Hall mobility of n-type samples was found to be much lower than for p-type materials, resulting in higher electrical resistivity values. However, the large electron effective mass translated into high Seebeck coefficient, up to 600 $\mu V.K^{-1}$ for n-type samples compared to only up to 200 $\mu V.K^{-1}$ for p-type samples. The experimental temperature variations of the electrical resistivity and the Seebeck coefficient of some binary skutterudites are shown in Figures 4 and 5, respectively. Minority carrier concentration effects (high mobility holes) are responsible for the change in Seebeck coefficient from positive to negative at high temperatures for n-type $CoSb_3$ and $IrSb_3$ samples (Figure 5). Because of a smaller band gap, this compensation occurs at lower temperatures in $CoSb_3$.

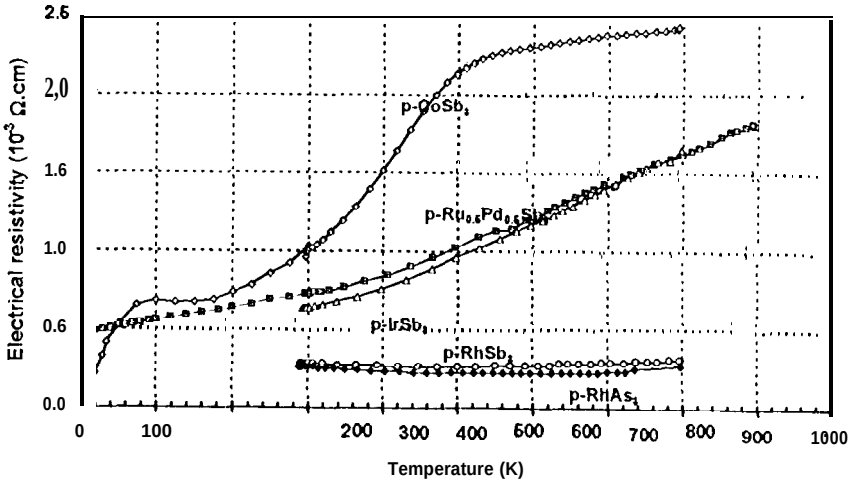


Figure 4: Electrical resistivity as a function of temperature for several n-type and p-type skutterudite compounds.

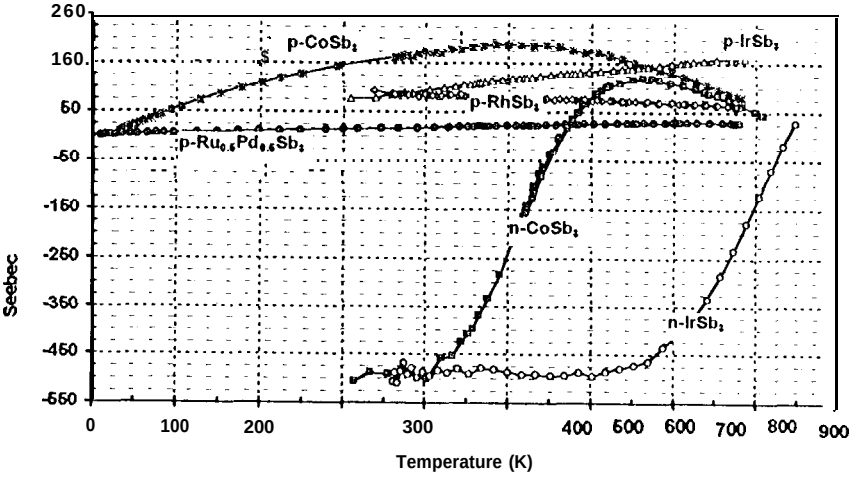


Figure 5: Seebeck coefficient as a function of temperature for several n-type and p-type skutterudite compounds

The thermal conductivity of p-type $CoSb_3$, $RhSb_3$ and $IrSb_3$ samples was measured from 10 to 800K (Figure **6).** The room temperature thermal conductivity of these three compounds ranges from 11 to 13 $W.m^{-1}.K^{-1}$ depending on the carrier concentration level, These values are quite reasonable considering their relatively high decomposition temperatures and bandgaps.

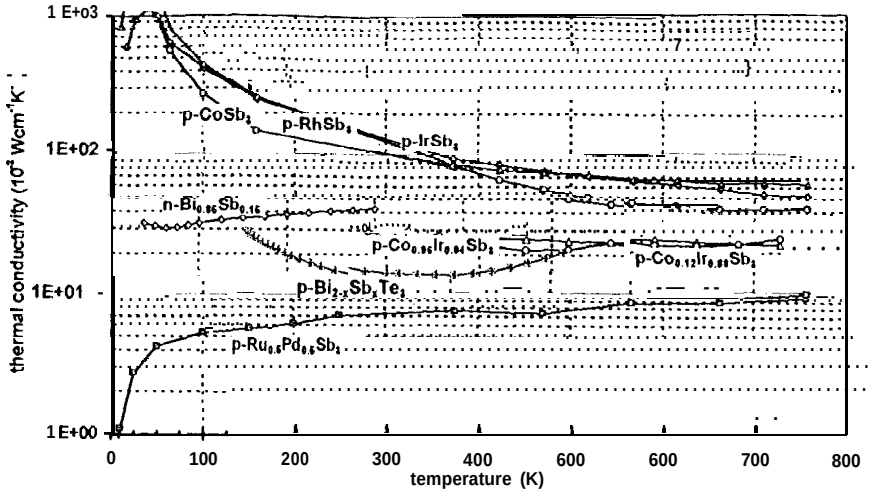


Figure 6: Thermal conductivity as a function of temperature for several n-type and p-type skutterudite compounds, solid solutions and related phases.

More information on the other binary compounds will be needed in order to show how the influence of bandgap and decomposition temperature impact on the thermal conductivity. However, because of the relatively high thermal conductivity values measured on the antimonide compounds, it appears unlikely that high ZT values will be obtained with just the binary compounds. Experimental and theoretical results on p-type $IrSb_3$ show that a maximum ZT value of 0.4 can be obtained at 900K [11,12]. These results are illustrated in Figure 7.

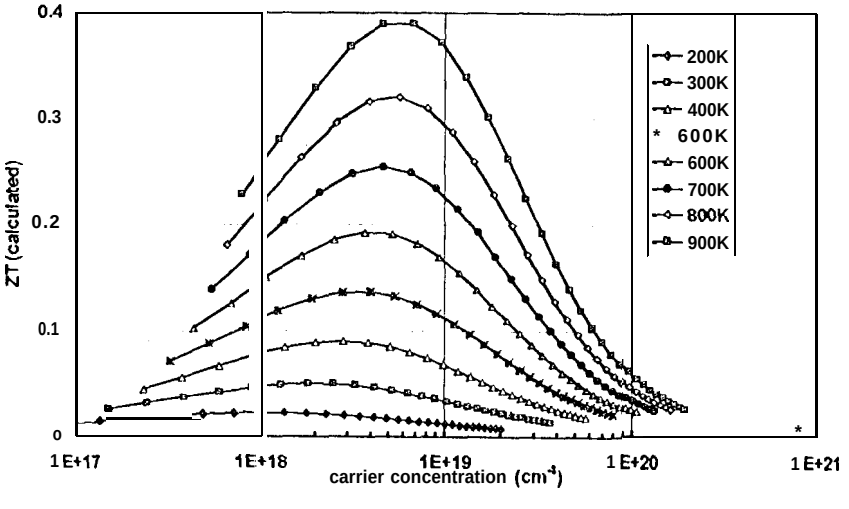


Figure 7: Calculated ZT values as a function of carrier concentration at different temperatures for p-type $IrSb_3$ (from reference [12]).

SOLID SOLUTIONS OF SKUTTERUDITES

The Wiedemann-Franz law can be used to calculate the lattice thermal conductivity of p-type $CoSb_3$, $RhSb_3$ and $IrSb_3$ samples For a carrier concentration of a 1 $x10^{19}$ cm^{-3}, calculations show that about 90% of the total thermal conductivity is due to the lattice contribution. In order to obtain high ZT values, the lattice thermal conductivity needs to be substantially reduced. Solid solutions possess a much lower lattice thermal conductivity due to atomic mass and volume fluctuations. However, a higher phonon scattering rate always has some negative impact on the carrier mobility, but because the drop in thermal conductivity is usually larger than the degradation of the electrical properties, ZT values are overall substantially improved. This process has been used for all the state of the art thermoelectric materials, and is of interest for skutterudite compounds.

The only solid solutions between binary skutterudite compounds reported in the literature show that CoP_3 and $CoAs_3$ form a complete range of solid solutions which obey the Vegard's rule and that the system $CoAs_{3-x}Sb_x$ has a miscibility gap in the region of x = 0.4 to 2.8 [13]. Work by us on $CoSb_3$-$IrSb_3$ compositions also demonstrated that a partial range of solid solutions exist in this system [14]. Thermal conductivit y measurements of several samples alloyed with 10 mol% $CoSb_3$ (or $IrSb_3$) showed that the thermal conductivity y dropped to about 3 $W.m^{-1}.K^{-1}$ at room temperature, a value 3 to 4 times smaller than for the individual compounds. These very encouraging results are also reported in Figure 6. Additional work conducted by us on other systems indicate skutterudite solid solutions, at least in some limited range of composition, are widespread.

SKUTTERUDITE RELATED PHASES

In natural skutterudite ores, cobalt is often partially replaced by nickel and iron [15], The substitution limit in the skutterudite systems $Fe_xCo_{1-x}As_3$ and $Ni_xCo_{1-x}As_3$ has been studied [16]. In the system systems $Fe_xCo_{1-x}As_3$, $0 \leqslant x \leqslant 0$. 16 and it was found that the substitution of cobalt by iron decreases the resistivity. For iron concentrations higher than 10/0, the conduction becomes n-t ype and iron is a donor. The homogeneity limit of the phase $Ni_xCo_{1-x}As_3$ is larger and $0 \leqslant x \leqslant 0.65$. Nickel behaves as a donor impurity and the resistivity of the samples decreases with increasing substitution. The conduction is p-type for $CoAs_3$ and becomes n-type with 10/0 substitution of nickel for cobalt. These examples show skutterudite related phases can be formed by substitution by neighboring atoms for the anion or the cation in binary skutterudite compounds, the condition being that the valence-electron count remains constant. A

certain number of these compounds was reported in the literature and are listed in Table 1, where a_o is the lattice parameter and 'f_n, is the decomposition temperature. Some of our results have also been included.

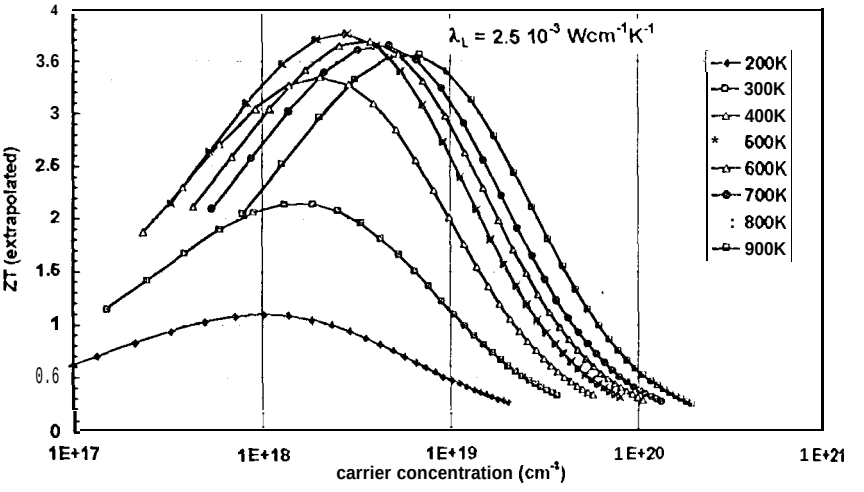
Table 1: Known skutterudite related phases

Composition	a. (Å)	T", (°C)	reference
$CoGe_{1.5}S_{1.5}$	8.0170	1000	17
$CoGe_{1.5}Se_{1.5}$	8.2990	800	17
$RhGe_{1.5}S_{1.5}$	8,2746	>800	18
$IrGe_{1.5}S_{1.5}$	8.297	>800"	18
$IrGe_{1.5}Se_{1.5}$	8.5591	>800"	18
$IrSn_{1.5}S_{1.5}$	8.7059	>800"	18
$Fe_{0.5}Ni_{0.5}Sb_3$	9.0904*	729*	19
$Fe_{0.5}Ni_{0.5}As_3$	8.2560	?	16
$Ru_{0.5}Pd_{0.5}Sb_3$	9,2960*	647*	20
$PtSn_{1.2}Sb_{1.8}$	9.3900	?	21

* our findings

The substitution can occur on the anion site ($CoAs_3$ -> $CoGe_{1.5}Se_{1.5}$) or on the cation site ($CoSb_3$ ->$Fe_{0.5}Ni_{0.5}Sb_3$). Structurally related skutterudite phases can also be formed by partial substitution of the cation or the anion ($IrSb_3$ -> $PtSn_{1.2}Sb_{1.8}$).

Almost no information about thermal and electrical properties of such phases is available in the literature, As well as for solid solutions, it is expected that the lattice thermal conductivity of these phases would be lower than for binary compounds. Some experimental results obtained on the $Ru_{0.5}Pd_{0.5}Sb_3$ composition are displayed in Figures 4, 5 and 6. It can be seen that both materials are heavi 1 y doped semiconductors. The p-type Hall mobility of $Ru_{0.5}Pd_{0.5}Sb_3$ is actually very good considering the complexity of the crystal structure. Figure 6 shows that the thermal conductivity of $Ru_{0.5}Pd_{0.5}Sb_3$ has a glassy behavior, decreasing with decreasing temperatures, At room temperature, the thermal conductivity value is 0,7 $W.m^{-1}.K^{-1}$, about 15 times lower than in $RhSb_3$ (or $IrSb_3$). This is also lower than the values obtained for the state of the art thermoelectric materials. The lattice contribution is estimated to 2.5-3 $W.m^{-1}.K^{-1}$, which is an extremely low value. However, this unoptimized material is still too heavily doped and the carrier concentration must be reduced to achieve larger Seebeck coefficient values, These results demonstrate the great potential of skutterudites for high ZT values as very high mobility and very low lattice thermal conductivity can be obtained with materials of the same crystal structure,



To illustrate this potential, the temperature dependent lattice thermal conductivity of p-type $IrSb_3$ has been replaced with the temperature dependent lattice thermal conductivity of $Ru_{0.5}Pd_{0.5}Sb_3$ and the ZT values shown on Figure 7 were recalculated and are plotted in Figure 8. It can be seen that the new ZT_{max} now approaches 3.7 at 500K. Of course,, it cannot be expected that there will be no degradation in electrical properties but this example shows that if the high mobility of the binary skutterudite compounds can be somewhat preserved, large reductions in thermal conductivity could lead to ZT values substantially larger than 1.

FILLED SKUTTERUDITES

The composition of these types of compounds can be represented by the formula LnT_4Pn_{12} (Ln = rare earth, Th; T = Fe, Ru, 0s; Pn = P, As, Sb). In these compounds, the voids which are formed in the TPn_3 (- T_4Pn_{12}) framework are filled with a cation and thus these compounds are a filled-up version of the skutterudite structure. A large number of these materials have already been synthesized (see for example [22-25]). While most of these compounds are metallic, it has been shown that some of them such as UFe_4P_{12} and CeF_4P_{12} are semiconductors [22]. The addition of a new ion(s) in the voids could be an efficient phonon scattering center and could result in substantially lower lattice thermal conductivity values, The properties of such skutterudite compounds remain to be fully characterized and such materials might also show some interesting potential.

CONCLUSION

A new family of promising thermoelectric materials with the skutterudite crystal structure has been presented. A number of binary compounds, solid solutions, related phases and filled skutterudite structures have been briefly reviewed, The possibilities of finding candidates for a particular operating temperature are great

in such a large family of materials. Initial results obtained on some of their representatives demonstrate the great potential of skutterudites for high ZT values as very high mobility and very low lattice thermal conductivity can be obtained with materials of the same crystal structure. In particular, that if the high mobility of the binary skutterudite compounds can be somewhat preserved, there are several approaches for large reductions in thermal conductivity that could lead to ZT values substantially larger than 1.

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